purified isophthalic acid

Processing Unsaturated Polyesters Based on Isophthalic Acid

Unsaturated polyesters based on isophthalic acid (isopolyesters) provide high strength and resiliency in a variety of applications, from structural automotive parts to sleek boat hulls. You can use isopolyesters in hand lay-up and spray-up, casting, sheet molding (SMC), bulk molding (BMC), injection molding, resin transfer molding (RTM), reaction injection molding (RIM), centrifugal casting, pultrusion, and filament-winding.

Isopolyesters designed for corrosion resistant applications combine excellent physical properties with outstanding resistance to various acids, solvents, and other chemicals. Another advantage of isopolyesters is that the resin can be pigmented, filled, and fiber-reinforced while it is still in a liquid form.

In the unsaturated polyester industry, BP is a major supplier of raw materials such as isophthalic acid, terephthalic acid, and maleic anhydride. Styrene monomer is a widely used reactive diluent for unsaturated polyesters. While BP does not commercially produce unsaturated polyesters, our technical services laboratory is constantly searching for new applications and better processing techniques for the use of our products in unsaturated polyesters.

The guidelines in this brochure will help you synthesize high quality polyester resins and reduce processing time.

bp

Contents

Overview of Polyester Processing

Polyesterification is a reversible condensation reaction with water as a by-product. Almost all polyester resins are formulated with an excess of hydroxyl groups.

You can increase the reaction rate by:

- Raising the temperature of the reactor,
- Improving agitation, and
- Using an efficient method of water removal; removing by-product water from the reaction shifts the equilibrium toward the polyester end product.

At the end of the reaction, the polyester is blended with inhibited styrene or some other reactive monomer. Free radical initiators (sometimes called catalysts) are used to start a free-radical reaction which causes the styrene to crosslink with the unsaturated functional groups in the polyester to form a solid thermoset plastic.

Some of the raw material variables that can affect the final properties of the polyester resin are use of different difunctional acids, different glycols, and different levels of styrene. These items are covered in detail in Bulletin PIA-70 “How ingredients influence unsaturated polyester properties,” available from your BP sales representative.

Equipment for Processing Unsaturated Polyester Resins

You need the following equipment to process unsaturated polyester resins:

- Reactor with agitator, heater, thermal sensors, inert gas sparge, raw material addition ports, and sample taps
- Partial condenser
- Total condenser
- Distillate receiver
- Blending tank for thinning the finished resin

BP's laboratory is equipped with 2 liter and 4 liter glass vessel bench scale reactors and with 10 gallon (38 liter) and 60 gallon (230 liter) pilot plant reactors. Diagrams of the bench and pilot scale reactors we use are shown in Figures 1 and 2.

Figure 1: BP's 2 Liter Bench Scale Reactor

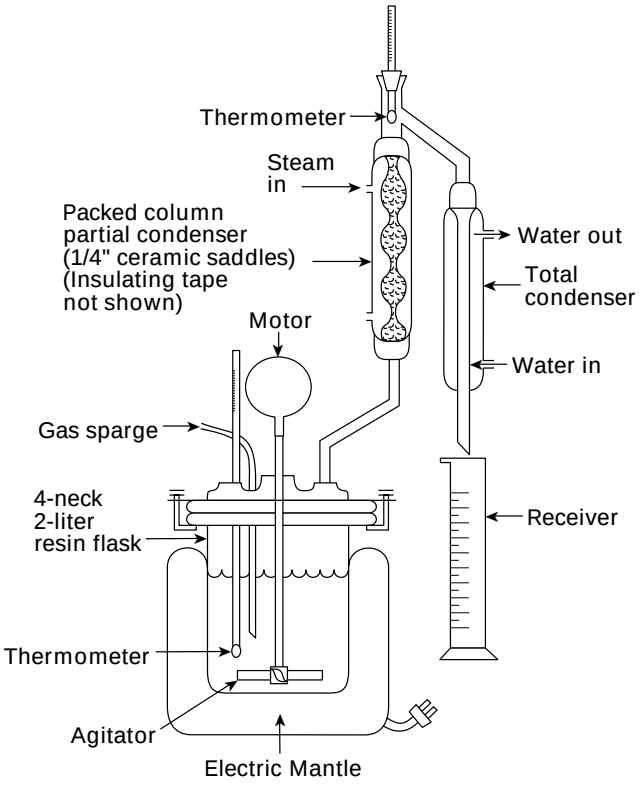
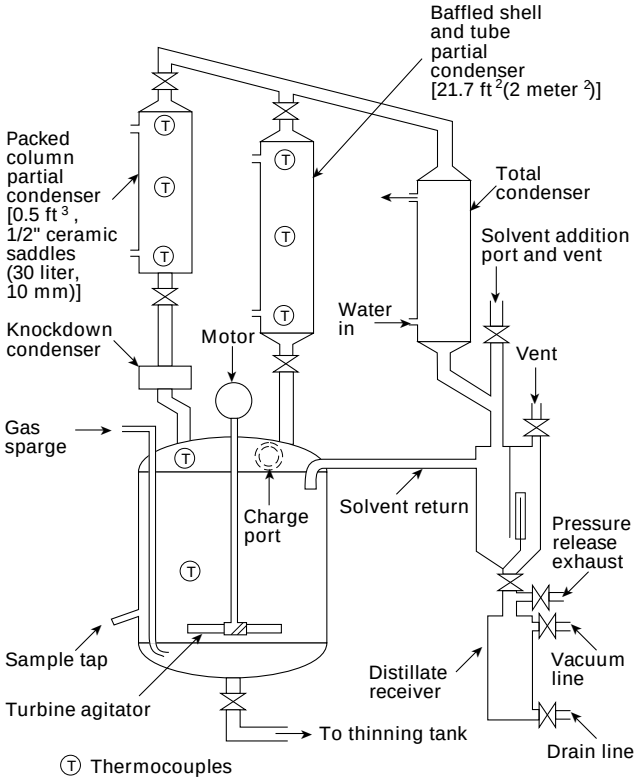


Figure 2: BP's 60 Gallon (230 liter) Pilot Plant Reactor



CAUTION: Pressure processing and vacuum processing requires equipment (reactors, condensers, and receivers) rated for high pressures. Consult your equipment manufacturer, insurance underwriter, and organizations such as the American Society of Mechanical Engineers and National Board of Boiler and Pressure Vessel Inspectors to develop stringent safety guidelines.

Reactors

The polyesterification reactor should be constructed of materials that will not corrode or contaminate the reaction mixture. 316 stainless steel and glass are often used. (The special requirements of pressure processing are covered on page 9.)

The reactor should be designed to agitate the ingredients thoroughly. Thorough agitation is required to prevent hot spots from discoloring the resin and to promote contact between the powdered acid and liquid glycol. BP's pilot plant reactors have the following equipment:

- Variable speed turbine blade agitators that maintain tip speeds of 200 to 1000 ft/min (1 to 5 meter per second)
- Mechanical foam breakers attached to the top of the agitators
- Baffles on the reactor wall that promote turbulence

The reactor should have adequate heating capacity. BP's 60 gallon (230 liter) reactor has a heating capacity of 75 MBtu/hr (100 watt per liter). This allows rapid heating and shorter processing times.

To prevent color-producing oxidation reactions, an inert gas sparge of nitrogen or some other inert gas should be bubbled through the reaction mixture. The inert gas should contain less than 20 ppm (and preferably less than 10 ppm) oxygen. Near the end of the reaction, this gas sparge helps remove the last traces of water. The sparge rate typically used in our 60 gallon reactor is 0.1 to 0.3 scf/min (0.2 to 0.6 ml/sec air flow per liter reactor capacity).

There should be raw material addition ports for the reactor and sample taps in the reactor and the distillate receiver.

Partial Condensers

The polyester reactor should be topped by a partial condenser. The partial condenser separates water from the glycols and returns the higher boiling components to the reactor. The separation within the partial condenser is controlled by the efficiency of the vapor-to-liquid mass transfer, the efficiency of the cooling surface, and the size of the condenser.

There are two kinds of partial condensers commonly available, a baffled tube condenser and a packed column condenser. In general, for a given volume, baffled tube condensers provide better separation but are more expensive than packed column condensers. (In order to run comparative experiments, BP's pilot plant reactor is topped with both kinds of partial condensers.) The packed column has a precondenser below it and a short total condenser above it. We prefer controlling the short precondenser.

You should carefully monitor the temperature profile of the partial condenser. As a minimum, you should measure the temperature at the top, middle, and bottom of the column. More measurement points provide a more accurate temperature profile.

By monitoring the temperature profile of the partial condenser, you can maintain separation efficiency while avoiding flooding. The temperature at the top of the partial condenser should remain slightly above the boiling point of water at reactor pressure.

As the reaction progresses, changes occur in the composition and temperature of vapors rising from the reactor. Therefore, you may need to adjust column conditions to maintain sufficient separation. As the reaction end point nears, you can help strip the evolved water by increasing the temperature of the jacket (by changing the jacket medium from hot water to steam). Or if you are using pressure rated equipment, you can apply a vacuum.

Table 1 gives the boiling points of pure components at 1 atm and at 50 psig (100 kPa and 445 kPa).

Table 1: Boiling Point of Pure Components

	Boiling Point, °C	
	at 1 atm (100 kPa)[1]	**at 50 psig (445 kPa)[1]**
Water	100	148
Propylene Glycol	189	215
Ethylene Glycol	198	230
Dipropylene Glycol	230	285
Diethylene Glycol	245	310
2-Methyl-1,3-Propane Diol	213	–-
Neopentyl glycol	210 sublimes	–-

[1] Absolute pressure on reactor.

The baffled tube condenser on BP's 60 gallon (230 liter) reactor (at 1 atm pressure) can be jacketed with hot water or low pressure (5 psig or 135 kPa) steam. A hot water (99°C or 210°F) jacket on the baffled tube condenser results in shorter processing times and less glycol loss than a low pressure steam (108°C or 227°F) jacket.

As shown in Figure 3, a hot water jacketed partial condenser provides dramatic reductions in processing times compared to low pressure steam. The greater heat capacity of hot water allows more heat to be applied to the reactor without flooding the partial condenser. In BP's equipment this permits about 10°C higher reactor temperatures.

The data in Figure 4 indicates that the better heat transfer of a hot water jacketed partial condenser also reduces glycol loss.

Figure 3: Effect of Jacket Medium and Condenser Type on First Stage Processing Time*

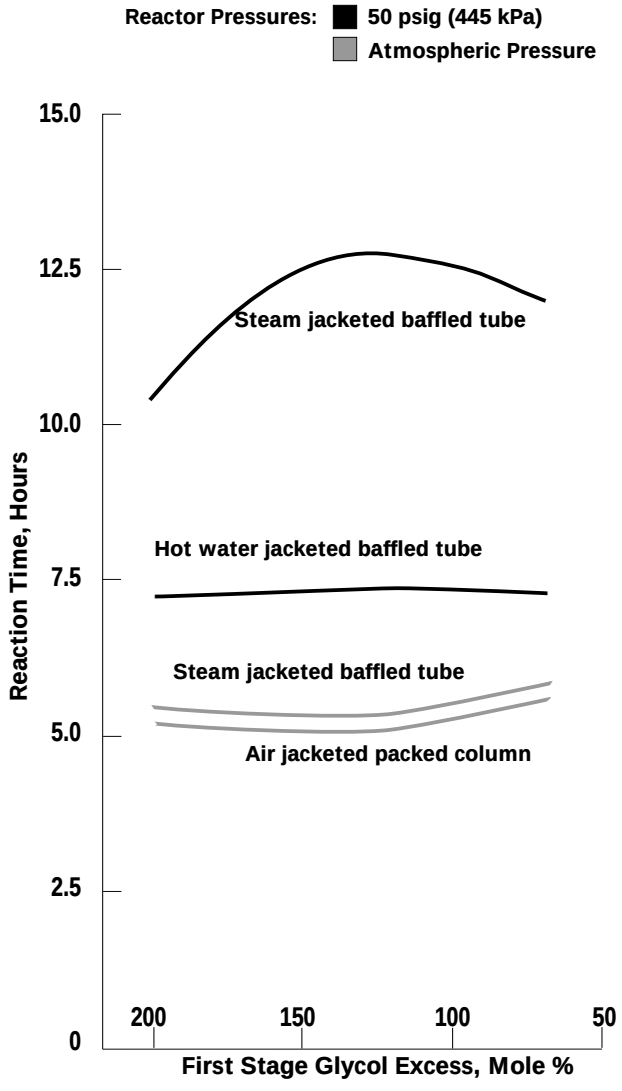
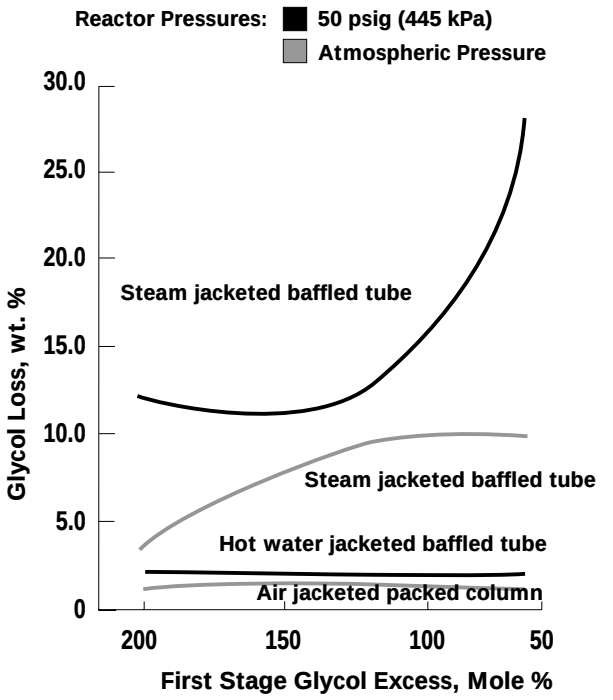


Figure 4: Effect of Jacket Medium and Condenser Type on First Stage Glycol Loss*



[1] Absolute Pressure.

*Data in Figures 3 and 4 are from isophthalic acid/propylene glycol resins processed in BP's 60 gallon (230 liter) reactor during first stage of full 2-stage method. Results using other types of resins, reactors, or methods will differ.

Blending Tanks

The hot resin should be blended into styrene in a separate blending tank rather than in the reactor. By using a separate blending tank, you free the reactor for the next polyester batch, minimize the risk of gel, and reduce the need for cleaning. The blending tank should meet the following specifications:

- It should be at least twice as large as the reactor to allow for diluting the resin to 50% NVM.
- It should have heating and cooling capacity.
- It should have an agitator capable of handling viscous materials.
- It should have baffles, which will improve mixing of viscous materials.
- The tank and transfer lines should be vented through a total condenser to prevent vapor emissions. Transfer lines should be heated if the tank is far from the reactor.

Table 8 on page 15 gives instructions for blending polyesters into styrene.

Processing Isophthalate Polyesters

There are three ways to make isophthalate polyesters. The quickest way is to use a one-stage method. With this method, add all the ingredients at once in a one-stage reaction. This is not the preferred method for processing unsaturated isopolyesters.

The full two-stage method produces top quality resins with outstanding corrosion resistance and high heat deflection temperature.

The modified two-stage method also produces high quality resins. It does so with a shorter processing time while retaining much of the physical properties of the full two-stage method.

One-Stage Method

With the one-stage method, charge all the ingredients to the reactor at once and heat to a maximum of 230°C (450°F) until the reaction is complete.

In the one-stage method, the unsaturated acid (which is more reactive than the isophthalic acid) forms a prepolymer with the glycol. The isophthalic acid and remaining glycol build onto this basic chain. The result is a polymer that has good physical properties and moderate chemical and heat resistance. The one-stage method is not recommended when processing high quality isopolyester resins.

Full Two-Stage Method

By using the full two-stage method, isopolyesters with excellent physical properties, resistance to chemicals, and high heat deflection temperature can be produced. These resins also have the best property retention after exposure to boiling water.

In the full two-stage method, isophthalic acid is first reacted with the glycols until a low acid number (less than 10 mg KOH/g) is reached. This constitutes a prepolymer. Then the unsaturated acid (or anhydride) is added to the reactor and the reaction is completed.

Table 2 provides instructions for a full two-stage esterification.

Table 2: Instructions For a Full Two-Stage Esterification

First Stage

1) Charge the glycol to the reactor kettle, sparge with inert gas and start heating and stirring. Charge isophthalic acid when the glycol is approximately 50°C (120°F). Seal the kettle and continue the inert gas sparge.

2) Fill the partial condenser jacket with hot water. Heat the reaction mass with highest heat input. The reaction will begin at around 180°C (360°F). Maintain heat on kettle and a slow water flow in condenser jacket until reaction reaches desired first stage properties as judged by reaction water collected or by acid number. During this stage the overhead temperature should stay near 100°C (210°F).

Second Stage

3) Determine the glycol lost during the first stage by analyzing the refractive index of the distillate or measuring the excess distillate over theoretical water of reaction. (See Figure 8, page 14 for the relationship between refractive index and percent glycol in water.) Charge sufficient glycol to make up for first stage loss.

4) The first stage reaction mass should be cooled below 155°C (320°F) before maleic anhydride or fumaric acid is added.

5) After the unsaturated acid or anhydride and any make-up glycol or second-stage glycol have been added, seal the kettle and resume heating. During the second stage maximum temperature should be 230°C (450°F). If resin color is critical, the maximum temperature should not exceed 210°C (410°F).

6) When the reaction end point nears (see "End Point" section on page 13) the partial condenser may be bypassed to rapidly remove residual moisture. If the lowest possible acid number is desired, however, the fractionation column should be used until the desired properties are reached.

7) Determine acid number and viscosity.

8) When esterification is complete, blend the resin into inhibited styrene (see guidelines in Table 9, page 15).

Modified Two-Stage Method

Polyesters formed by the modified two-stage method (U.S. patent 3,252,941; BP) have many of the same physical properties as those formed by the full two-stage method, but reaction times are much shorter.

The second stage of the modified two-stage method is conducted the same way as it is in the full two-stage method. However, with the modified two-stage method, you begin the second stage after the isophthalic acid has undergone half-ester formation. This occurs at an acid value of about 60 for most isopolyesters. It is also evidence that a half-ester has been formed when a sample of the reaction mix forms a clear pill when cooled to room temperature. At that point, the unsaturated acid is added. This early addition avoids the long processing time of a conventional first stage. Various studies have indicated that the best balance of processing time and resin properties is obtained by introducing the second stage component when between 75% and 90% of theoretical distillate has been collected. As a result, you may shorten the first stage and the overall reaction time by several hours.

During the first stage, two indicators will help you determine when to add the unsaturated acid:

1. Check the distillate water volume. Consider glycol losses as inferred from refractive index measurement (see page 14).

2. Check the clarity of a sample of cool resin. To test clarity, drop a small sample of the resin onto a cold smooth surface. After the resin cools to room temperature it should form a clear pill, indicating that there are no free crystals of isophthalic acid. You should add the unsaturated acid when a sample of the reaction mass forms a cold, clear pill.

Isopolyester Formulations and Properties

Table 3 shows several sample isopolyester formulations and lists the results of tests conducted by BP to show how different processing methods can affect reaction time and resin properties.

In general, a resin produced by the full two-stage method took longer to process than by the one-stage method but has higher heat resistance. A resin produced by the modified two-stage method had a higher deflection temperature, and slightly longer processing time. Flexural, tensile, and hardness were not significantly affected.

Formulations containing a high isophthalic acid/ maleic anhydride ratio (resin SG-35) benefited more from the two-stage methods than those with lower ratios (resins SG-30 and 3482).

Table 3: Unsaturated Polyester Formulations*

Materials*	Tough Resin SG-35 Mole Ratio	Tough Resin SG-35 by wt	Corrosion Resistant SG-10 Mole Ratio	Corrosion Resistant SG-10 by wt	Compression Molding SG-303482 Mole Ratio	Compression Molding SG-303482 by wt	Tough Resin "Classic" Mole Ratio	Tough Resin "Classic" by wt
Isophthalic Acid	2.0	48.8	1.0	38.5	1.0	19.6	3.0	31.3
Ethylene Glycol	—	—	—	—	—	—	1.75	6.8
Propylene Glycol	3.3	36.8	2.2	38.8	3.0	26.9	—	—
Diethylene Glycol	—	—	—	—	—	—	5.6	37.3
Dipropylene Glycol	—	—	—	—	1.2	18.9	—	—
Maleic Anhydride	1.0	14.4	1.0	22.7	3.0	34.6	4.0	24.6
Total Charge	—	100.0	—	100.0	—	100.0	—	100.0
Less 1st Stage Water	-4.0	-5.3	-2.0	-8.3	-2.0	-4.2	-6.0	-6.8
Less 2nd Stage Water	-1.0	-2.6	-1.0	-4.2	-3.0	-6.4	-4.0	-4.5
Yield		92.1		87.5		89.4		88.7

Properties**	SG-35	SG-10	SG-30	3482
Total Processing Time, hr***				
1-Stage	22.2	17.5	12.5	12.0
Full 2-Stage	22.4	23.8	12.3	20.5
Modified 2-Stage	21.0	19.5	9.8	20.1
Deflection Temperature, °C				
1-Stage	75	91	121	80
Full 2-Stage	84	105	126	84
Modified 2-Stage	85	101	120	83

* All resins prepared in BP's 4-liter glass reactor. All resins at 60% NVM in styrene monomer.

** Samples were cast unreinforced and unfilled.

*** Heat-up and cool-down times are not included.

Time Saving Variations

Through extensive research, BP has developed techniques for reducing the processing time of isopolyesters. By using these or other techniques, you can save manufacturing time, reduce energy and labor costs, and increase resin plant capacity.

These techniques include:

- Raising reactor pressure,
- Using catalysts,
- Adding a prepolymer heel to the first stage, which increases the reaction rate by increasing contact between the isophthalic acid and glycols.

Pressure Processing

One technique for reducing processing time is to raise the reaction temperature. You accomplish this by increasing the reactor pressure which raises the boiling point of the water/glycol mixture. The polyesterification reaction occurs more rapidly at temperatures of 210 to 230°C (410 to 450°F).

Figure 5 shows how higher temperatures can reduce first-stage processing times by 35 to 65 percent. Table 4 shows how higher pressures raise the boiling points of pure components. Figure 4 on page 5 shows that reactions at high pressure also appear to have lower glycol losses.

Pressure processing does not affect the physical properties of finished resins and works best with two-stage processing of propylene glycol resins. Pressure processing does not significantly affect reaction time in the one-stage method.

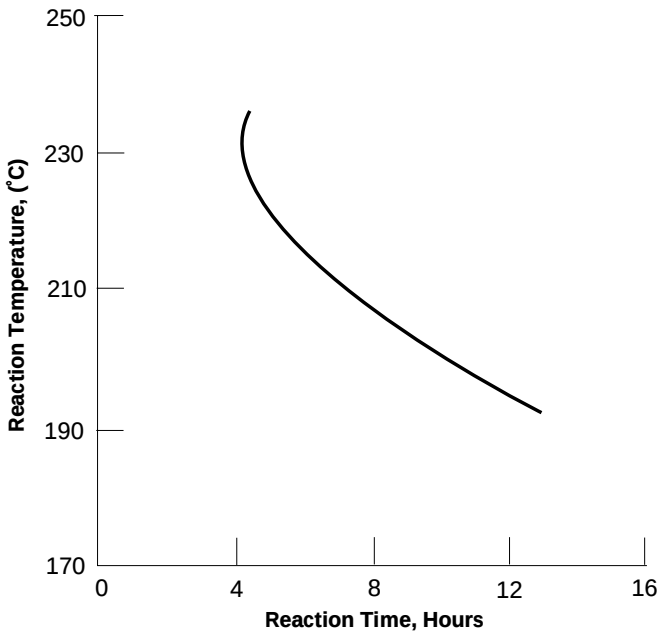
Building initial pressure with the volatiles best coordinates pressure with temperature during the early phase. Then maintaining inert gas sparge throughout the reaction is the preferred method of pressure processing. Pressurizing the whole system rather than just the reactor is preferred. If just the reactor is pressurized, there will be high glycol losses.

Table 4: Boiling Point of Pure Components

	Boiling Point, °C	
	atm Pressure (100 kPa)[1]	at 50 psig (445 kPa)[1]
Water	100	148
Propylene Glycol	189	215
Ethylene Glycol	198	230
Dipropylene Glycol	230	285
Diethylene Glycol	245	310
2-Methyl-1,3-Propane Diol	213	–-
Neopentyl Glycol	210 sublimes	—

[1]Absolute Pressure

Figure 5: Time Savings Using Pressure Processing



CAUTION: Pressure processing and vacuum processing requires equipment (reactors, condensers, and receivers) rated for high pressures. Consult your equipment manufacturer, insurance underwriter, and organizations such as the American Society of Mechanical Engineers and National Board of Boiler and Pressure Vessel Inspectors to develop stringent safety guidelines.

Reducing pressure late during the second stage (about 90% completion) effectively draws a vacuum and can strip the remaining reaction water and decrease glycol losses. While no time reduction results, the apparent vacuum does produce lower acid numbers. Inert gas sparge flow continues during the pressure reduction.

Table 5a lists procedures for pressure processing using a reactor topped with a steam-jacketed baffled tube condenser. Table 5b lists procedures for pressure processing using a reactor topped with a packed column condenser.

Table 5a: Pressure Processing Using BP's 60 Gallon Reactor with Steam-Jacketed Baffled Tube Condenser

1. Charge kettle and start cook as with conventional processing. Steam heat condenser.
2. Close reactor system below the receiver and use expanding gases (water and glycol) to build pressure. In this way, pressure and temperature increase compatibly to allow expedient removal of the large quantity of water evolved early in the reaction.
3. Maintain sparge rate at 50-100 standard cm^3/s and open system through receiver enough to maintain pressure with sparge flow.
4. Control kettle heat input to maintain desired head temperature.
5. When head temperature starts to drop, increase steam pressure to 40 psig (280 kPa) and increase kettle temperature to 230°C (446°F).

   Sparge flow can also be increased, but receiver must be opened more to compensate and maintain pressure.
6. When within 15 units of the desired acid number, discontinue heat in-put to allow the temperature to decrease below 205°C (400°F). Pressure will fall, acting as a vacuum to help remove the last remaining water of reaction.
7. Add the second stage glycol, glycol makeup and the unsaturated acid or anhydride and continue processing as with a conventional cook.

Table 5b: Pressure Processing Using BP's 60 Gallon Reactor with Packed Column Condenser

1. Charge kettle and start cook as with conventional processing.
2. Close reactor system below the receiver and use expanding gases (water and glycol) to build pressure. In this way, pressure and temperature increase compatibly to allow expedient removal of the large quantity of water evolved early in the reaction.
3. Maintain sparge rate at 50-100 standard cm^3/s and open system through receiver enough to maintain pressure with sparge flow.
4. Set kettle for maximum heat input.
5. Monitor column's temperature gradient and overhead temperature. When flooding threatens, cool the distilling vapors with a brief burst of water in the knock-down tube below the packed column.
6. When head temperature starts to drop and maximum reactant temperature has been achieved, sparge flow can be increased but the receiver must be opened more to compensate and maintain pressure.
7. When within 15 units of the desired acid number, discontinue heat in-put to allow the temperature to decrease below 205°C (400°F). Pressure will fall, acting as a vacuum to help remove the last remaining water of reaction.
8. Add the second stage glycol, glycol makeup and the unsaturated acid or anhydride and continue processing as with a conventional cook.

Esterification Catalysts

Several catalysts to accelerate the first-stage reaction of isophthalic acid with propylene glycol have been studied by BP. Catalysts have been found to be effective when used in processing at atmospheric pressure, but not in pressure processing. Some catalysts may darken the resin (Gardner 5 versus Gardner 1 for an uncatalyzed control). Thorough testing is recommended before using any catalyst on a commercial scale.

Table 6 lists the results of tests using *Fascat*® 4100 in isophthalic acid/propylene glycol resins prepared in BP's 4 liter reactor. Figures 6a and 6b present these data graphically. Catalyst levels of .010 to .025 wt % were most effective in decreasing processing time while retaining the resin's chemical resistance.

Figure 6a shows that as you increase the amount of catalyst, processing time drops sharply at first, but then flattens out as you continue to add more catalyst. Figure 6b shows that the flexural strength of resin in boiling water after 48 is not strongly dependent on catalyst level. Larger differences occur after immersion in boiling water for 144 hours. Resins with the lowest levels of catalyst had the best hydrolytic stability (least susceptible to crazing).

Figure 6a: Effect of Catalyst Level on Full 2-Stage Processing Time*

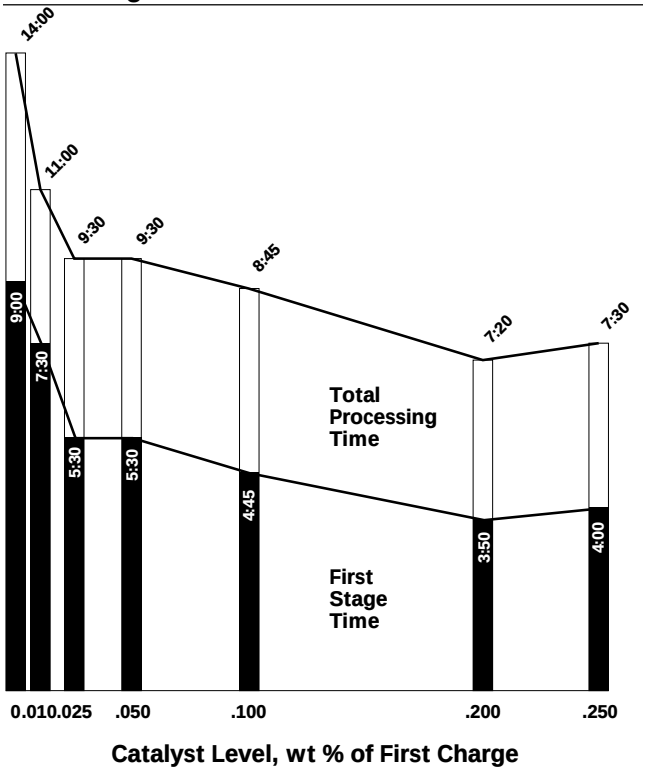
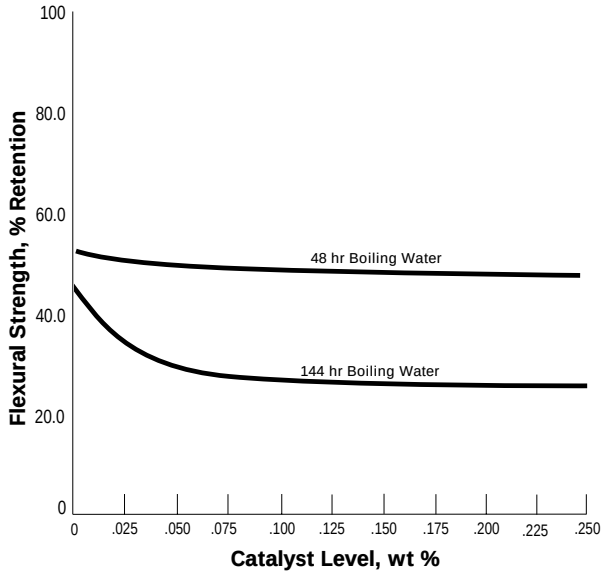


Figure 6b: Effect of Catalyst Level on Flexural Strength Retention*



Fascat® 4100, trademark of Elf Atochem, Rahway, NJ 07065, telephone 201-499-0200.

* Data in Figures 6a and 6b are from Table 6.

Table 7 shows the time savings that are possible when other catalysts are used in isopolyester resins made from isophthalic acid and propylene glycol.

Using a Prepolymer Heel

You can increase efficiency in the first stage by using a prepolymer "heel" from a previous batch. To do this, save a portion of a finished first stage in a holding tank for use as a heel in the next first stage. This heel can reduce synthesis time by acting as a soluble base for the isophthalic acid. Time reductions are closely related to the proportion of heel used in the first stage. It is questionable whether this approach affects overall capacity.

Table 6: Effect of Catalyst Level on Resin Properties*

	Catalyst Level, wt % of First Stage Change						
	0[1]	**.010**	**.025**	**.050**	**.100**	**.200**	**.250**
Processing Time							
First Stage, hr:min	8:45	7:30	5:30	5:30	4:40	3:50	4:00
Second Stage, hr:min	4:45	3:30	4:00	4:00	4:15	3:30	3:30
Total, hr:min	13:30	11:00	9:30	9:30	8:55	7:20	7:30
Acid Number, mg KOH/g	24.1	24.9	24.7	23.6	23.8	23.5	24.1
Viscosity at 65% NVM, mPa-s (cP)	1450	1620	1460	1040	1120	1740	1300
Flexural Strength							
48 hr Boiling Water, %	51.3	58.5	55.0	45.0	47.5	48.2	48.7
144 hr Boiling Water, %	44.9	41.1	33.6	20.4	27.8	27.6	22.7

* Data in Table 6 is from isophthalic acid/maleic anhydride/ propylene glycol resins processed in BP's 4 liter reactor using the full 2-stage method and Fascat 4100 catalyst. Results using other types of resins, reactors, and methods will differ.

[1] Average of two runs.

Table 7: First-Stage Time Savings Using Various Catalysts*

	none[1]	**A**[1]	**B**[1]	**none**[2]	**B**[2]	**C**[2]	**none**[2]	**D**[2]	**none**[3]	**E**[3]
Final Acid Number	6.1	9.8	5.9	8.3	6.9	6.8	8.3	9.6	10.2	9.4
Reaction Time, hr:min	20:25	17:50	13:45	8:55	5:45	7:05	9:25	7:00	10:05	8:40
Time Savings, % of Control	—	13.0	33.0	—	36.0	21.0	—	25.7	—	14.0

* Data in Table 7 is from isophthalic acid/propylene glycol resins processed in BP's 4 liter reactor during first stage of full 2-stage method. Results using other types of resins, reactors, or methods will differ.

Catalyst types:

A — 0.2 wt % tetra-isopropyl titanate
B — 0.2 wt % tetrabutyl titanate
C — 0.1 wt % tributyl phosphate
D — 0.20 wt % stannous oxalate and 0.07 wt % sodium acetate
E — 0.65 wt % stannous oxalate

Catalyst measured as wt % of initial charge.

[1] 120 mole % excess glycol with baffled tube condenser.
[2] 120 mole % excess glycol with packed column condenser.
[3] 110 mole % excess glycol with packed column condenser.

Finishing the Polyester Resin

The previous sections described different methods of processing polyesters. This section tells how various reaction parameters relate and describes how to blend the polyester with the styrene monomer.

As the polyesterification reaction progresses, molecular weight and viscosity increase while hydroxyl number and acid number decrease. The proper end point for the reaction depends on the application. For instance, a corrosion resistant resin requires a low acid number and high molecular weight.

BP does not recommend adding glycol to the resin when the acid number is below 50 (or within two hours of reaction end) in the final stage. Doing so may result in poor quality resin.

Determining End Point

Viscosity and acid number are two commonly used tests to monitor progress of synthesis. They can be run quickly, allowing their use as a control variable during resin processing. The tests are described in the following documents:

- Acid number is described in ASTM D1639.
- Viscosity is described in SPI Resins Technical Committee Test Procedures AF-145. (Note: Cone and plate viscosity is also useful.)

Molecular weight and hydroxyl number tests are difficult to measure quickly and are not used as control variables. Rather, they are used to characterize the resin after processing is complete.

- Hydroxyl number is described in ASTM E222 Method B. End group number is the sum of acid number and hydroxyl number.
- Number average molecular weight is determined by vapor phase osmometry. The procedure is described in ASTM D3592.

For resin formulations frequently produced in the same reactor, you can develop a table or graph showing resin properties versus time. Such a graph can help you predict end-point time and improve quality control. After creating the graph, you only need to measure viscosity and acid number to monitor the reaction.

Figures 7a-7d show acid number, hydroxyl number, viscosity, and molecular weight during the final hours of producing resin SG-10 (from Table 3) with the full two-stage process. These graphs apply only to

Figure 7a: Acid Number

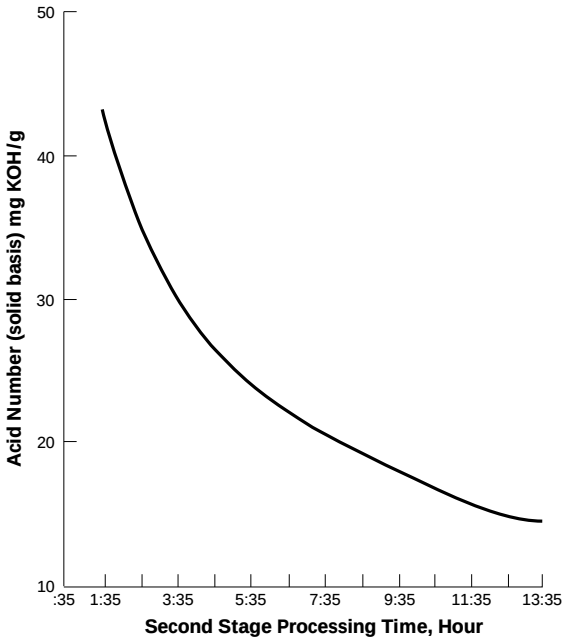
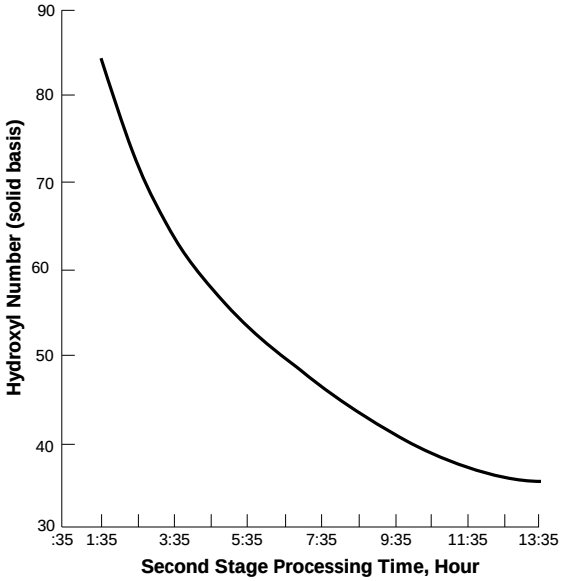


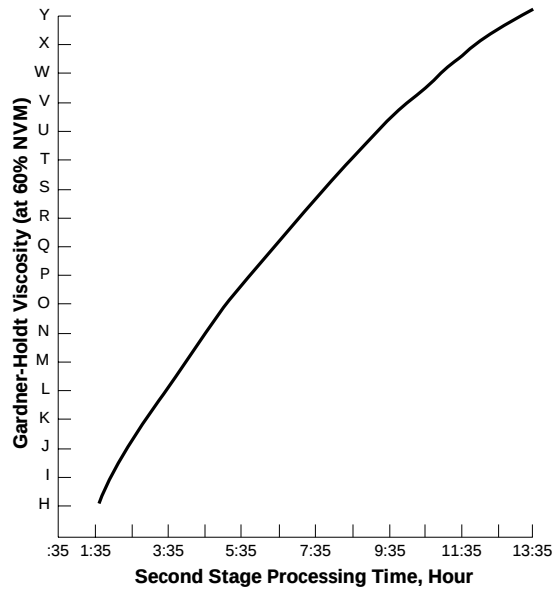
Figure 7b: Hydroxyl Number



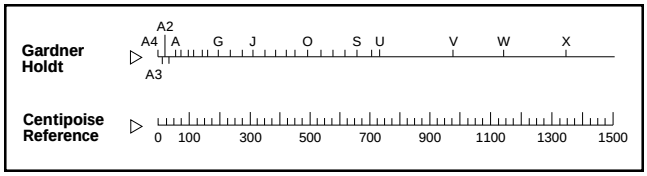
ASTM documents may be obtained by writing to: American Society of Testing and Materials, 1916 Race St., Philadelphia, PA 19103-1187, 205-299-5400.

SPI documents may be obtained by writing to: Society of the Plastics Industry, 1275 K Street N.W., Suite 400, Washington, DC 20005.

Figure 7c: Gardner-Holdt Viscosity



Viscosity conversion reference for Figure 7c



batches of resin SG-10 produced in BP's 60 gallon (230 liter) reactor using a baffled tube partial condenser. Different formulations, reactors, and processing conditions will produce different results.

Determining Glycol Loss

In the absence of contaminants, glycol loss can be calculated by measuring the refractive index of the distillate to determine the water/glycol ratio. Figure 8 shows how to determine glycol concentration from refractive index measurements.

Blending Isopolyesters into Monomer

Styrene is the most common reactive diluent used to produce unsaturated polyesters. Blending isopolyesters into styrene requires some care since styrene has a boiling point of 145°C (295°F) while many molten isopolyesters must be heated above that point to keep them flowing.

Figure 7d: Molecular Weight

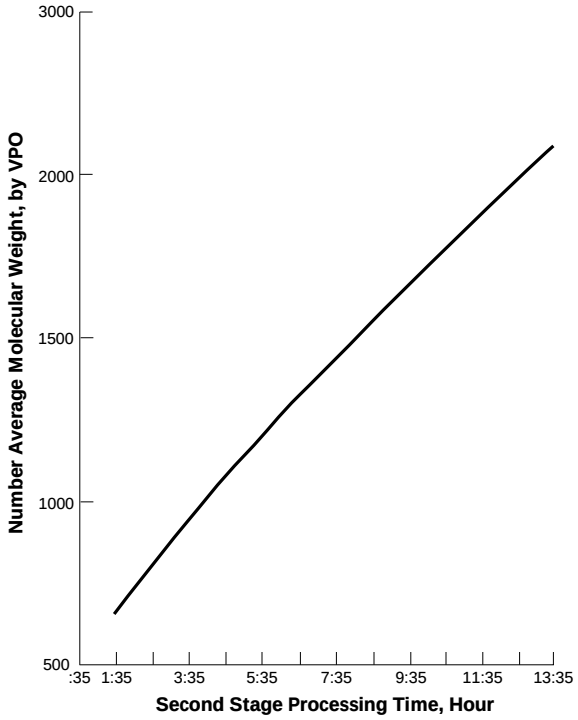


Figure 8: Determining Glycol/Water Ratio from Refractive Index

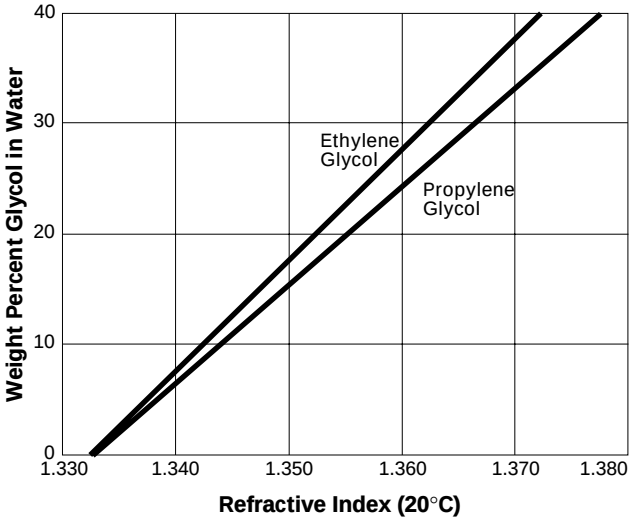


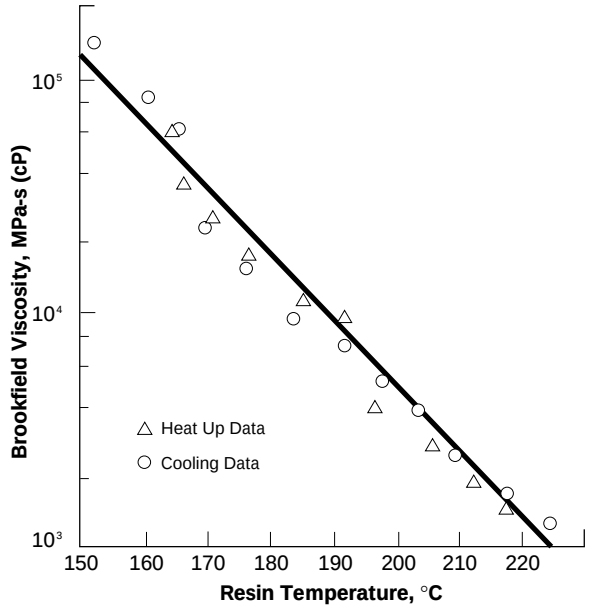
Table 8 provides instructions for thinning isopolyesters with styrene. The hot resin should be slowly added to styrene. Resin and/or styrene must be stabilized with thinning inhibitors before dilution.

Table 8: Instructions for Blending Isopolyester into Styrene

1. Inhibit styrene and add to blending tank; heat to 70°C (160°F).
2. Cool isopolyester resin below 205°C (400°F) and add inhibitor.
3. Transfer the resin to a well agitated blending tank.
4. As the resin enters the blending tank, start cooling the water in the jacket. Keep the blending tank temperature below 80°C (175°F). If necessary, reduce the flow of resin into the tank to control temperature.
5. After complete mixing and cooling to below 32°C (90°F), filter the resin-styrene solution and transfer it to storage.

Before dilution, you must keep resin SG-10 near 180°C (355°F) so it can flow through transfer lines to the blending tank. Figure 9 illustrates the relationship between temperature and molten viscosity for this resin.

Figure 9: Viscosity of Undiluted Isopolyester vs. Temperature*



* Resin SG-10 processed to a Gardner-Holdt viscosity of Z at 60% solids in styrene.

Appendix

Equivalent Weights

Table 9 shows the equivalent weights of commonly used materials in formulating unsaturated polyesters.

Table 9: Equivalent Weights of Commonly Used Materials

	Equivalent Weight
Difunctional Acids/Anhydrides	
Fumaric Acid	58
Isophthalic Acid	83
Maleic Anhydride	49
Phthalic Anhydride	74
Terephthalic Acid	83
Trifunctional Acids/Anhydrides	
Trimellitic Anhydride	64
Tetrafunctional Acids/Anhydrides	
Pyromellitic Dianhydride	55
Difunctional Alcohols	
1,3–Butanediol	45
1,4–Butanediol	45
Cyclohexanedimethanol	72
Diethylene Glycol	53
Dimethylol Propionic Acid	67
Dipropylene Glycol	67
Ethylene Glycol	31
2-Methyl-1,3-Propane Diol	45
Neopentyl Glycol	52
1,5–Pentanediol	52
Propylene Glycol	38
Tetraethylene Glycol	97
Triethylene Glycol	75
Trimethylene Glycol	38
Trimethyl Pentanediol	73
Trifunctional Alcohols	
Glycerine, 99%	31
Trimethylol Ethane	41
Trimethylol Propane	45

Trouble Shooting Guide

Poor ResinColor

Possible Causes	Suggested Remedies
Low Quality Inert Gas	Inert gas sparge must contain less than 20 ppm oxygen, and preferably less han 10 ppm. Many oxygen determining devices are not sensitive to this low evel of oxygen contamination.
High Reactor Temperature	Use the full 2-stage or modified 2-stage processing method to reduce the time unsaturated acid is exposed to high temperatures. Color formation studies suggest that unsaturation of maleic anhydride or fumaric acid is necessary in the color-producing reaction. If extremely light colored polyesters are required, use a maximum kettle temperature of about 210°C (410°F) in the second stage. Add 250-1000 ppm of triphenyl phosphite at the beginning of the second stage to aid in reducing color formation.
Poor Agitation	With some formulations, the initial charge of isophthalic acid and glycol can form a thick slurry, which easily collects on the baffles or high on the side walls of the kettle. If this slurry remains on the walls, it can "char" during a rapid heat-up. To control this problem, improve agitation and/or add baffles to the kettle. "Hot spots"A reaction kettle with localized "hot spots" can cause resin discoloration, especially when combined with poor agitation. To control this problem, eliminate hot spots and improve agitation.
Contaminants	Traces of caustic left from cleaning can cause severe color degradation and even lead to premature gelation. Protect raw materials from contamination by using proper storage and transferring facilities. Various raw material suppliers can provide additional recommendations.
Oxygen Entering the Reactor	Oxygen can enter the reactor during vacuum operations if reactor is not perfectly sealed.

Processing Time Too Long

Possible Causes	Suggested Remedies
Inadequate Heat Supply	An inadequate heat supply causes excessively long heat-up periods, especially with stepwise processing techniques requiring multiple heat-up periods. Establish an adequate heat supply to realize the benefits of a good partial condenser system. Increase the sparge rate 3 to 4 times the initial rate during final two hours of the reaction.
Poor Agitation	Improve agitation. Increase the rate of inert gas sparge to inadequate inert gas remove water of esterification. Any water of esterification or excess sparge rate glycol remaining in the sparge rate resin can also hinder viscosity build-up.
Inadequate Partial	Make sure that the partial condenser is designed to accommodate the condenser additional water of esterification produced when processing isopolyesters. Inadequate condenser capacity can cause high glycol losses and can retard removal of water of esterification. Slow water removal, in turn, lowers the rate of reaction. (See the section on "Partial condensers" on page 4.)

Inadequate Cooling	Cooling time has a significant effect on the total processing time. Use cooling coils instead of a cooling jacket since they provide a larger surface for heat transfer. If the coils are equipped to operate on both water and steam, you can also use them in the initial heating of the batch. Resin can sometimes "freeze"(become immobile) on cooling surfaces, thus interfering with the cooling process. In this case, alternately cool and stop the cooling process to allow the resin on these surfaces to remelt and be dispersed.
Poor Agitation	Improve agitation. Increase the rate of inert gas sparge to inadequate inert gas.
Too Much Glycol Excess	Formulations with too high an excess exhibit rapid acid number decrease and lengthy processing may be required to achieve the desired viscosity. Reduce the glycol excess to reduce processing time.
Too Little Glycol Excess	Formulations with too low an excess exhibit a rapid viscosity and an extremely slow acid number decrease; for these, the desired acid number may be unattainable within the desired viscosity range. Increase the glycol excess to reduce processing time.
General	Use the time savings variations suggested in this brochure: Pressure processing (page 9), Esterification catalysts (page 11), Prepolymer heel (page 12).

Hazy Resin

Possible Causes	**Suggested Remedies**
Styrene Polymerization	Polystyrene is insoluble in polyester resins and will show up as a haze in the product. Eliminate polystyrene contamination. You can test for this contamination qualitatively by diluting the styrene monomer with ten volumes of dry methanol. Any turbidity is an indication of polymer.
High Acid Number	In general, process isopolyesters to an acid number of 10-25. Isopolyesters with acid numbers over 30 can yield hazy resin solutions when blended with styrene.
Too Much Ethylene Glycol	Isophthalate polyester resins made with substantial amounts of ethylene glycol can produce hazy solutions when blended with styrene monomer. The amount of ethylene glycol the formulation will tolerate depends on the amount of isophthalic acid present: the more isophthalic acid the less ethylene glycol. For most formulations, limit the glycol portion to less than 30 mol % ethylene glycol.
Resin Contamination	Various polyester resins are not compatible with each other. Storage of incompatible resins in the same tank can result in haze. You should clean finished resin storage facilities between batches; or investigate the compatibility of different resins before storage.
General	The following techniques help reduce haze in laboratory prepared resins: 1. Increase glycol in the first stage. If some glycol is withheld from the first stage, try charging more or all of it. If all glycol is charged initially, try charging the amount typically lost during the first stage. 2. Cook to a slightly higher first stage acid number. 3. Reduce the first-stage processing time.

High Acid Number

Possible Causes	Suggested Remedies
Insufficient Glycol Excess	An unusually high acid number is obtained when the formulation contains insufficient glycol excess. You can usually solve the problem by increasing the amount of glycol excess. However, you must be careful not to obtain a lower acid number at the expense of significantly increasing the hydroxyl number of the finished polyester resin.
High Glycol Loss	The loss of a significant portion of the glycol can cause an unusually high acid number. Review the remedies under "High glycol losses."
Incomplete Reaction	A polyester resin which has not been processed to its required viscosity will have a high acid number. If the reaction is slow, review the remedies under "Processing time too long."

Low Acid Number

Possible Causes	Suggested Remedies
Too Much Glycol Excess	You usually obtain a low acid number when the formulation contains too much glycol excess. To control this problem, decrease the glycol excess until you obtain an acid number in the desired range.

Low Viscosity

Possible Causes	Suggested Remedies
Too Much Glycol Excess	Insufficient viscosity build-up can result from too much glycol excess. The usual signs of this problem are low viscosity and extremely low acid number. Decrease glycol excess until viscosity is in the desired range.
Incomplete Reaction	If the reaction is too slow, review the remedies under "Processing time too long."

High Glycol Losses

Possible Causes	Suggested Remedies
Inefficient Partial Condenser	See the section on "Partial condensers" on page 4.
Sparge Rate Too High	Excess gas flow through the reactor will draw off glycol. Adjust the sparge rate so that it does not exceed 0.6 ml/sec air flow per liter reactor volume.

High Hydroxyl Number

Possible Causes	Suggested Remedies
Too Much Glycol Excess	A high glycol excess tends to yield resin with a high hydroxyl number. It is important to choose a glycol excess that will yield the desired hydroxyl number range when processed to its required viscosity.
Incomplete Reaction	A polyester resin which has not been processed to its required viscosity will have a high hydroxyl number (and high acid number). If the reaction is slow, see remedies under "Processing time too long."

Additional References

For additional information on unsaturated polyester resin processing, request bulletins:

PIA-70 How Ingredients Influence Unsaturated Polyester Properties

PIA-86 Make Corrosion Resistant Unsaturated Polyesters with PIA

PIA-93 Evaluating Isopolyester Resins

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The product and uses described herein may require global registrations for chemical inventory listings, or for use in food contact or medical devices. For further information, send an e-mail to: bpcares@bp.com.

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BP
Sales Administration and Customer Service
150 West Warrenville Road
Naperville, Illinois 60563-8460
Toll-free: 877/701-2726
Fax: 630/961-7700

BP
Building A, Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LL
United Kingdom
Telephone: 44 (0) 1932 767627
Fax: 44 (0) 1932 767914

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